

LIQUID FUEL REFORMER DEVELOPMENT

C. Pereira , R. Wilkenhoener, S. Ahmed, and M. Krumpelt

Electrochemical Technology Program
Chemical Technology Division
Argonne National Laboratory
9700 S. Cass Avenue
Argonne, Illinois 60439

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C. Pereira , R. Wilkenhoener, S. Ahmed, and M. Krumpelt
Argonne National Laboratory
Argonne, IL 60439

Abstract

At Argonne National Laboratory we are developing a process to convert hydrocarbon fuels to a clean hydrogen feed for a fuel cell. The process incorporates a partial oxidation/steam reforming catalyst that can process hydrocarbon feeds at lower temperatures than existing commercial catalysts. We have tested the catalyst with three diesel-type fuels: hexadecane, low-sulfur diesel fuel, and a regular diesel fuel. We achieved complete conversion of the feed to products. Hexadecane yielded products containing 60% hydrogen on a dry, nitrogen-free basis at 800°C. For the two diesel fuels, higher temperatures, >850°C, were required to approach similar levels of hydrogen in the product stream. At 800°C, hydrogen yield of the low sulfur diesel was 32%, while that of the regular diesel was 52%. Residual products in both cases included CO, CO₂, ethane, ethylene, and methane.

Introduction

The Department of Energy's Hydrogen Program is involved with the development of remote power generation in the Arctic circle. The traditional means of power generation there has been through internal combustion engines. The fuel available at these remote locations is diesel. Recent developments of fuel cell power systems, which are more efficient and produce cleaner emissions, suggest that these systems, if adapted to operate with diesel fuels, can be used in the Arctic zone. Since fuel cells operate on hydrogen,

the use of fuel cells with diesel requires that it is possible to efficiently convert the diesel fuels into a hydrogen-rich gas.

The chemical process industry produces hydrogen in large amounts by the steam reforming process – where the hydrocarbon fuel is reacted with steam via an endothermic (heat absorbing) reaction. However, this process is better suited to large chemical plants, which have excess heat available from other processes. Furthermore, several problems with existing diesel-fuel reformer technology must be overcome. Catalysts tend to degrade over time. The high sulfur content of diesel poisons existing catalysts. Thermal cycling, particularly on start-up and shutdown, may lead to thermal shock. Extensive coke formation deactivates catalysts. High temperatures improve conversion, resulting in better system efficiency, but reduce material stability.

An alternative process is partial oxidation where the hydrocarbon fuel is reacted with air and steam to produce hydrogen. The heat effects of this reaction can be controlled directly by adjusting the feed proportions of fuel, air, and steam. Consequently, external heat sources are not required, and designs for partial oxidation reformers are simple, smaller, and lighter. The practice of partial oxidation reforming in the petrochemical industry is typically done in a two-step process – a high-temperature (1200°C) step where the complex hydrocarbons are broken down into simpler molecules (methane and oxides of carbon), followed by (catalytic) steam reforming of methane.

At Argonne National Laboratory, we are developing a process to convert hydrocarbon fuels to a clean hydrogen feed for a fuel cell. The process incorporates a partial oxidation/steam reforming catalyst that can process hydrocarbon feeds at lower temperatures than existing commercial catalysts. We have developed a partial oxidation/steam reforming catalyst that converts gasoline to hydrogen, carbon monoxide, and carbon dioxide at a lower temperature than existing commercial catalysts. We have demonstrated complete conversion of these feeds, producing enough hydrogen to potentially power a 5 kW fuel cell stack /1/.

The effluent from the fuel processor will require further treatment to remove carbon monoxide and sulfur and produce a suitable fuel cell feed. We are also developing more robust water-gas shift catalysts that will work better under transient operating conditions than current catalysts /2/. In addition, we are testing catalysts for preferential oxidation of CO and CO sorbents to treat the product stream.

In this paper we report results of tests with three diesel fuels: pure hexadecane, a low-sulfur diesel fuel, and a regular diesel fuel. All three of the feeds were processed over a single catalyst composition at a variety of temperatures. We were able to achieve complete conversion of the feeds to lower hydrocarbons and hydrogen. The products for all three feeds contained between 30 and 60% hydrogen on a dry, nitrogen-free basis at 800°C.

Experimental

Hexadecane was obtained from Aldrich Chemical Co. Certified low-sulfur diesel fuel, grade no. 1-D, was obtained from Phillips Petroleum Co. Regular diesel fuel, grade no. 2-D, was obtained from a local service station (nomenclature according to /3/). The fuels were not treated further. Properties of the fuels are given in Table 1. The partial oxidation catalyst was prepared in-house. The catalyst was placed in a 0.41 cm ID tubular reactor within a tube furnace. The bed height was approximately 2.5 cm. The temperatures at the top and bottom of the bed were monitored with thermocouples.

Table 1: Properties of Diesel Fuels Tested

Composition (wt.%)	Low Sulfur Diesel Grade No.1-D	Diesel Grade No.2-D
C	85.52	86.86
H	14.23	12.93
S	0.029	0.046
N	1 ppm-wt	227 ppm-wt
Distillation in °C*		
T10	194.3	217.9
T50	227.4	265.0
T90	260.4	325.7
Specific Gravity at 16°C	0.8141	0.8663

* T10, T50, T90 are the temperatures at which 10, 50, and 90% of the fuel is evaporated.

The fuel and water were fed into the top of the reactor, where they vaporized and mixed with the incoming oxygen and nitrogen, which acts as an internal standard. The liquid feed rates were controlled with high pressure liquid chromatography pumps; the gas flow rates were maintained with mass flow controllers. The reactant stream then passed over the catalyst, and the products were analyzed with a gas chromatograph. Pure oxygen was used in the reactant stream to improve the detectability of hydrocarbons that may be present in the product. The gas chromatograph could not be used to quantify water and heavy hydrocarbons. Therefore, we used the hydrogen-to-carbon (H/C) ratio to obtain an atom balance and approximate a mass balance.

Results and Discussion

Thermodynamic calculations were carried out to determine the feasibility and initial operating conditions for a diesel fuel reformer. Hexadecane ($C_{16}H_{34}$) was used as a surrogate for diesel fuel in the equilibrium calculations and in the initial feasibility studies to determine the viability of the process. Figure 1 shows the results of thermodynamic equilibrium calculations. It plots the equilibrium product gas

distributions obtained as a function of temperature, from the partial oxidation reforming of hexadecane. The O_2 -to-fuel ratio is 8, and the water-to-fuel ratio is 16. The hydrogen percentage is maximized at 700°C.

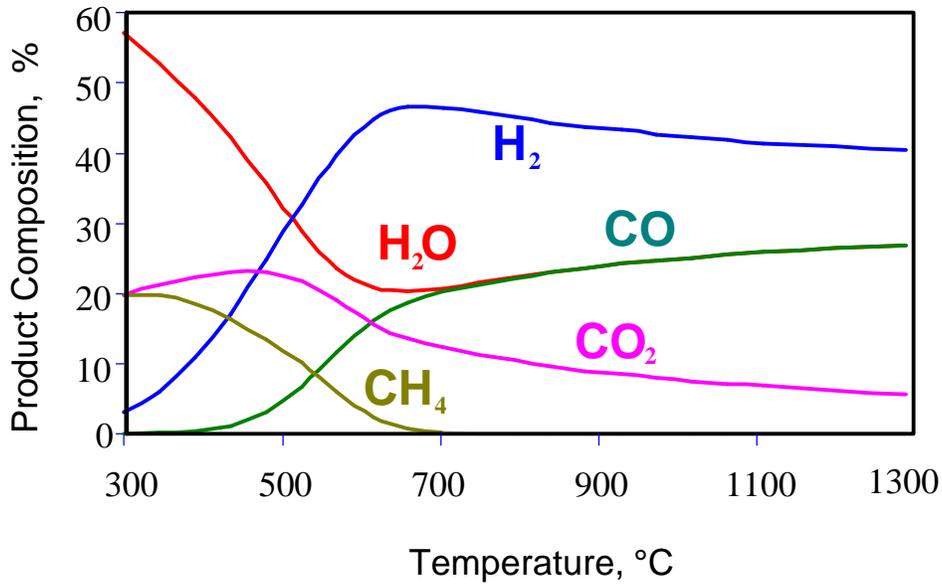


Figure 1: Equilibrium Calculation for Diesel Reforming

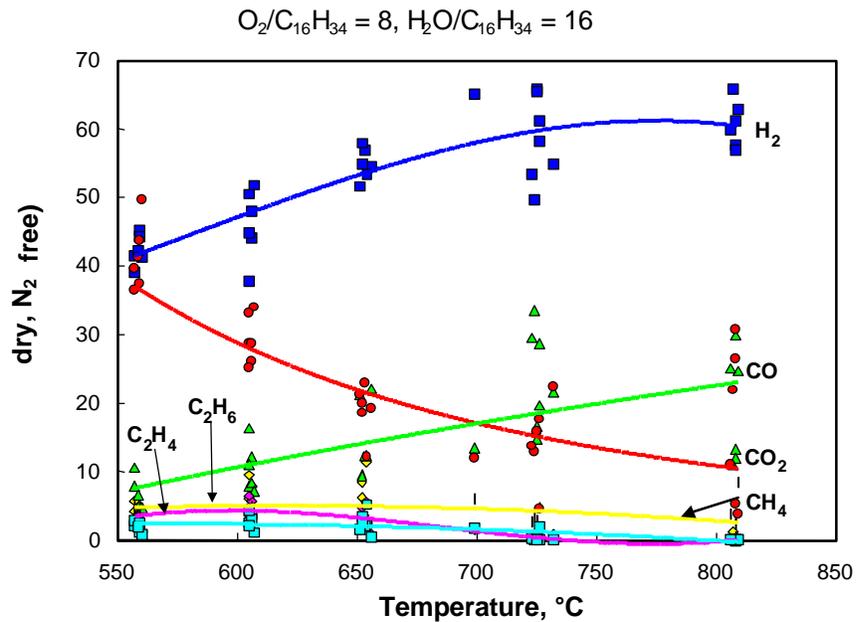


Figure 2: Effect of Temperature on Products from Hexadecane

Figure 2 shows the measured effect of temperature on the product distribution from the partial oxidation reforming of hexadecane. The feed consisted of 0.04 mL/min of liquid hexadecane, 0.04 mL/min of liquid water, and 24.5 mL/min of oxygen. The feed corresponds to an O₂-to-fuel molar volume ratio of 8, and a water-to-fuel molar ratio of 16.2. The gas hourly space velocity was 3700/h. The results are similar to the equilibrium product distribution in Figure 1. As can be seen in Figure 2, the hydrogen and carbon monoxide levels increase as the temperature is raised, while the carbon dioxide and methane levels decrease. Above 725°C, the hydrogen percentage in the product begins to level off at 60%. Raising the reactor temperature leads to a greater conversion of methane. The CO/CO₂ ratio increases with temperature due to the reverse water-gas shift reaction ($H_2 + CO_2 = CO + H_2O$), which is favored at high temperatures. At 800°C, undesirable byproducts such as ethane and ethylene are present in trace quantities. Although methane remains a significant product, the slope of the methane curve in Figure 2 indicates that it is not reduced significantly at higher temperatures.

The effect of temperature on the product distribution from the partial oxidation reforming is shown in Figure 3 for grade 1 diesel and in Figure 4 for grade 2. The O₂-to-fuel molar volume ratio was 8, and a water-to-fuel molar ratio was 24 for both tests. The higher water-to-fuel ratio was used to reduce coke formation with the diesel fuel, which has a lower H/C ratio than hexadecane.

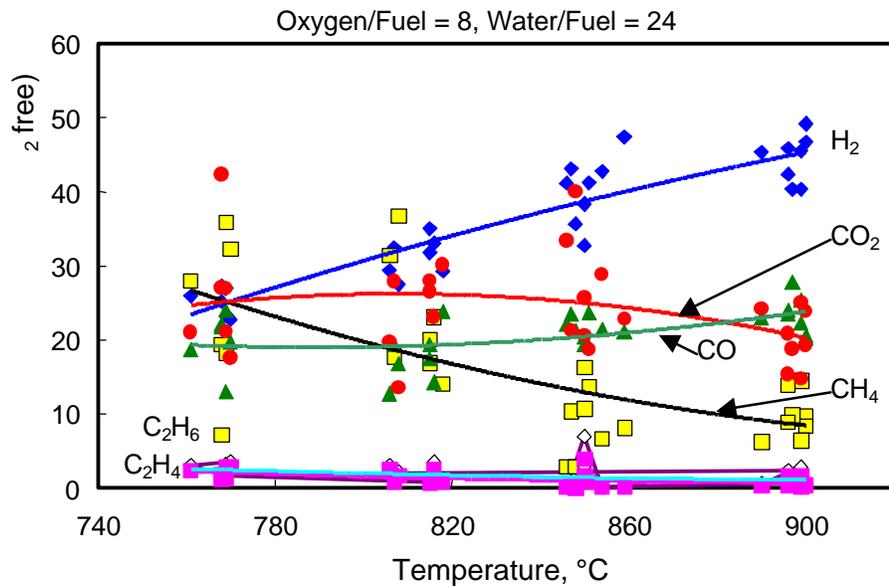


Figure 3: Effect of Temperature on Products from Grade 1 Diesel

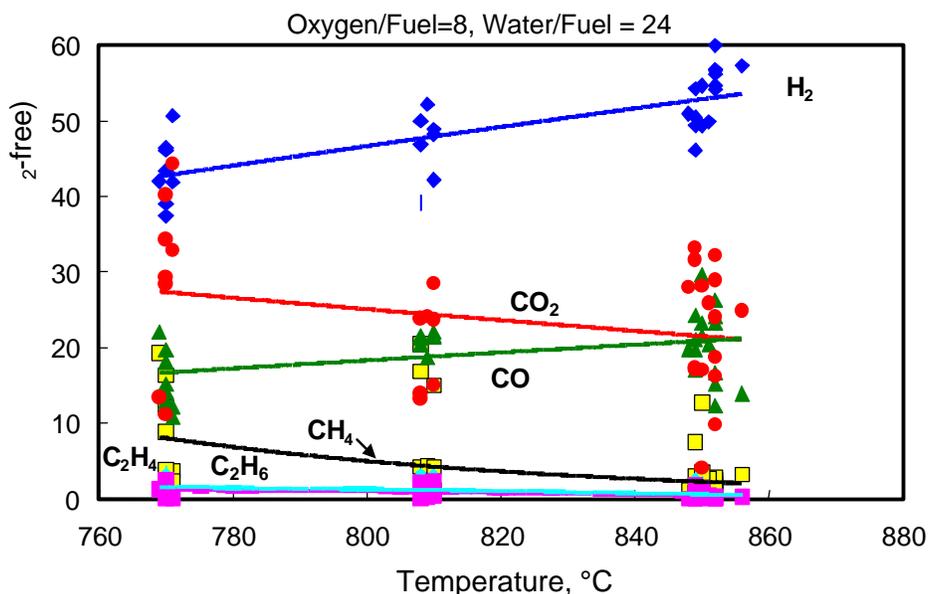


Figure 4: Effect of Temperature on Products from Grade 2 Diesel

As was the case for hexadecane, the hydrogen and carbon monoxide levels increase as the temperature is raised, while the carbon dioxide and methane levels decrease. However, conversion to hydrogen is significantly lower at similar reaction temperatures. An average product composition of 52% hydrogen is achieved at 860°C for grade 2 diesel. As with hexadecane, the CO/CO₂ ratio and methane conversion increase with temperature.

Figure 5 shows the product gas distributions for hexadecane and diesel grade no. 2, along with the distribution predicted from equilibrium calculations for hexadecane. The O₂-to-fuel ratio was 8 for all settings, while the water-to-fuel amount was 24 for the diesel conversion, 16.2 for the measured hexadecane conversion, and 16 for the calculated hexadecane conversion.

The measured product composition for the partial oxidation reforming of hexadecane contains slightly more H₂ and CO₂, but less CO than that predicted by equilibrium. This suggests that the selectivity of the catalyst favors the formation of hydrogen. The experimental product contained some methane, although equilibrium calculations indicate that none should be present. It is not known whether the methane is formed from secondary reactions among H₂, CO, and CO₂, or if methane is an intermediate product formed from the scission of hexadecane molecules.

The diesel fuel reformat contains less hydrogen than the hexadecane reformat, which is due in part to the lower H/C ratio of the grade 2 diesel (H/C =) vs. 2.1 for hexadecane. In addition, diesel reforming requires a slightly higher reforming temperature. Based on

these preliminary data., it appears that the Argonne catalyst can reform the complex hydrocarbons present in diesel at the relatively low temperatures of 850°C. This is significant because non-catalyzed partial oxidation reforming requires temperatures in excess of 1200°C to achieve similar conversions.

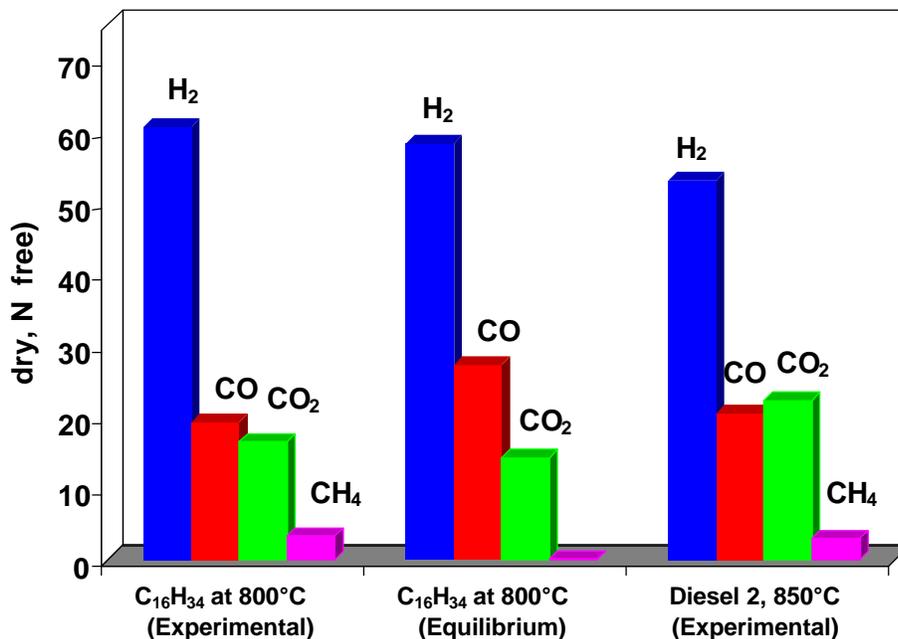


Figure 5: Product Composition for Hexadecane and Two Diesel Fuels

Comparing the results for the two grades of diesel fuel, we find that the hydrogen concentration in the product was actually higher for the grade 2 than for grade 1 diesel. This result is unexpected because grade 2 diesel has a higher fraction of aromatics than grade 1, as shown in Table 2. Aromatics tend to reduce the H/C ratio of the feed, and, consequently should result in a lower hydrogen yield. As expected, the diesel fuels also yield a larger fraction of hydrocarbon products, primarily methane.

Conclusions

The results demonstrate that the partial oxidation/steam reforming catalyst developed by Argonne can be used to produce hydrogen from diesel fuel. We were able to produce a product stream containing 60% hydrogen on a dry basis from hexadecane at 725°C. With actual diesel fuel, we produced a dry product containing 50% hydrogen at 850°C. We did see differences in product composition for the two grades of diesel

Table 2: Composition of Two Diesel Fuels (wt.%)

Compound	Low-Sulfur Diesel Grade No.1-D	Diesel Grade No.2-D
Paraffins	40	40
Cycloparaffins	30	10
Unsaturated Aliphatics	10	10
Aromatics	20	40
Sulfur	0.029	0.046

fuel that were tested. These differences likely arise from the differences in the composition of the fuels.

All tests with diesel have been short-term tests run in micro-reactors with catalysts originally designed to process gasoline. Production of hydrogen from diesel fuel comparable to that achieved with hexadecane may be achievable with modifications to the catalyst composition and structure. In addition, the catalyst materials must be resistant to degradation and deactivation because diesel fuel contains higher sulfur levels than gasoline and requires higher temperatures for reforming. In the tests run to date, we see no evidence of catalyst degradation or coking. However, the long-term thermal stability and sulfur tolerance of the catalysts must be determined. In order to demonstrate the effectiveness of the catalyst and overall fuel process, we plan to test the reformer in conjunction with post-processing components that will clean up the reformat to be suitable for use by a polymer electrolyte fuel cell. We also plan to demonstrate the reforming step at a larger scale.

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